

REMARKS

Claims 84-93 are pending in the Application

Claims 87-90 are withdrawn from consideration and cancelled herein.

Claims 84-86 and 91-93 are rejected.

Claims 84 and 91 are amended herein.

Claims 86 and 93 are cancelled herein.

Claims 94 and 95 are added herein.

I. RESTRICTION UNDER 35 U.S.C. § 121

Examiner has restricted Claims into two Groups: Group I (Claims 84-86 and 91-93) and Group II (Claims 87-90). Office Action at 2. Applicant confirms the election, without traverse, of Claims 84-86 and 91-93, belonging to Group I.

II. CLAIM OBJECTION

Examiner has objected to Claim 84 because it unnecessarily repeats the word “at.” Applicant has amended Claim 84 to remove the repeated word “at.” Applicant has likewise amended Claim 91 to remove the repeated word “at” in that claim.

In light of the foregoing, Applicant respectfully requests the Examiner withdraw his objection to Claim 84.

III. REJECTION UNDER 35 U.S.C. § 103(a) OVER *HIURA* IN VIEW OF *IJIMA*

Claims 84-86 and 91-93 are rejected under 35 U.S.C. § 103(a) as being unpatentable over *Hiura et al.*, United States Patent No. 5,698,175 (“*Hiura*”) in view of Iijima, et al., “Single-shell carbon nanotubes of 1-nm diameter,” *Nature*, Vol. 363, June 17, 1993, pp 603-605 (“*Iijima*”). Office Action, at 3.

The Examiner contends that “*Hiura* discloses a method for producing end-derivatized carbon nanotubes comprising the steps of: a) providing a plurality of carbon nanotubes with at

least about 100 carbon atoms; and b) reacting the carbon nanotubes with a compound that provides at least one substituent on at least one of the ends of least a portion of the carbon nanotubes (Abstract). At least one substituent is selected from the group consisting of alkyl; acyl; aryl; aralkyl; halogen; substituted thiol; unsubstituted thiol; substituted amino; unsubstituted amino; hydroxyl (Column 3). The derivatized carbon nanotubes are inherently soluble in some medium.” Office Action, at 3-4.

Regarding Claims 86 and 93, these claims have been cancelled. Therefore, the rejection of these claims is now moot.

Regarding Claims 84-85 and 91-92, Applicant respectfully traverses the rejection.

To establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art and not based on applicant’s disclosure. See M.P.E.P. 706.02(j); see also *In re Vaeck*, 947 F.2d 488, 20 U.S.P.Q.2d 1438 (Fed. Cir. 1991).

The Examiner has acknowledged that “*Hiura* does not expressly state that the carbon nanotubes are single-wall carbon nanotubes.” Office Action, at 4.

The fact that the processes disclosed in *Hiura* relate to **multi-wall** carbon nanotubes and not single-wall carbon nanotubes is critical because there are significant differences in terms of structure, properties and chemical reactivity between multi-wall and single-wall carbon nanotubes.

The distinction between single-wall and multi-wall carbon nanotubes is important because multi-wall carbon nanotubes are fundamentally different from single-wall carbon nanotubes. Single-wall carbon nanotubes are molecules of carbon, while multi-wall carbon nanotubes are assemblies of carbon. Single-wall carbon nanotubes have only a single layer of

sp^2 -hybridized carbon atoms generally arranged in hexagons and pentagons. Because of their single-layer, single wall carbon nanotubes generally cannot support defects in growth and are more susceptible to destruction by bond breakage or reaction. In contrast, multi-wall carbon nanotubes are composed of multiple, cylindrical concentric carbon layers arranged in a nested or scrolled fashion. Because of this arrangement, the carbon shells of multi-wall carbon nanotubes can withstand wall defects, which often appear as dislocations, kinks, holes, edges on the side-wall surfaces, *etc.* Also because of their multiple layers and the interconnections between these layers, multi-wall nanotubes can withstand much more rigorous chemical processing, physical conditions, and extensive chemical bond breakage without nanotube destruction compared to single-wall carbon nanotubes.

Single-wall carbon nanotubes “rope” together and are held tightly by van der Waals forces. As such, single-wall nanotubes are difficult to separate and disperse in other media, while multi-wall nanotubes do not share the same propensity to rope and, as such, are readily separable and dispersible. The structural differences between single-wall and multi-wall carbon nanotubes also leads to differences in physical and chemical properties, such as tensile strength, modulus, flexibility, thermal conductivity, electrical conductivity, chemical reactivity and chemical stability. As a result of such differences, the chemistry that can be done with each species is quite different and would be unpredictable.

Hiura primarily teaches the purification of multi-wall carbon nanotubes. Such purification is carried out by reacting such nanotubes with highly oxidative acids and/or oxidation agents under reflux and/or ultrasonic conditions. Such purification damages the multi-wall structures, as shown graphically in *Hiura* (Fig. 3). Application of the teachings of *Hiura* to multi-wall carbon nanotubes, typically riddled with defects, results in the breaking of carbon-carbon bonds generally at regions of defects on the walls as well as the ends. See *Hiura* at Figure 3. However, because of their multi-wall structure, the multi-wall nanotubes can withstand attack to their wall layers and still remain intact. As will be appreciated by one of skill in the art, such bond splitting with single-wall carbon nanotubes would be expected to result in destruction of the single-wall nanotubes. Hence, not only would the teachings of *Hiura*

when combined with the teachings of *Iijima* not have suggested a reasonable likelihood of success as applied to single-wall carbon nanotubes, such a chemical protocol would fail to achieve the desired results.

Rather than expect the process of *Hiura* to succeed with single-wall carbon nanotubes, it was reasonable to believe such processes would destroy the single-wall carbon nanotubes. Such an expectation was, in fact, widely held by those skilled in the art well after the publication dates of *Hiura* and *Iijima*, as is confirmed by Dujardin *et al.*, “Purification of Single-Shell Nanotubes,” *Adv. Mater.*, **10**, No. 8, 611-613 (1998) (“*Dujardin*”), attached as **Exhibit A**. *Dujardin* notes that “[i]t was believed that purification of single-shell nanotubes based on preferential oxidation and/or separation using surfactants was much more difficult than that of [multi-shell] nanotubes.” *Dujardin*, at 611. A reason for this was because “gas-phase oxidation, which yields purified multishell nanotubes, destroys the single-shell nanotubes before anything else in the sample.” *Id.* Accordingly, a person of ordinary skill would not have been motivated, nor had reason to expect success, in combining the methods of *Hiura* and *Iijima*. And, had a person of ordinary skill combined the references, the combination would not have resulted in the invention of the instant application recited in Claims 84-87 and 91-93.

Thus, not only would have it not been obvious to one of ordinary skill in the art to apply the processes of *Hiura* to the nanotubes of *Iijima* to achieve the end-derivatization of single-wall carbon nanotubes, one of ordinary skill in the art would have been discouraged to apply the processes of *Hiura* to the nanotubes of *Iijima* because there would not be a reasonable expectation of success.

Thus, as there is no suggestion or motivation in *Hiura* or *Iijima*, taken separately or together, or in the knowledge generally available to one of ordinary skill in the art, to modify the references or to combine reference teachings, and, furthermore, as there is no reasonable expectation of success were the references so modified, a *prima facie* case of obviousness is unsupported.

In light of the foregoing, Applicant respectfully requests that the Examiner withdraw the rejection of Claims 84-85 and 91-92 under 35 U.S.C. §103(a) as being unpatentable over *Hiura* in view of *Iijima*.

IV. NEW CLAIMS

Applicant has added Claims 94 and 95. No new matter is introduced by virtue of these additions. Support for these claims is found in the Application, at page 34, ll. 11-13.

V. CONCLUSION

As a result of the foregoing, it is asserted by Applicant that the Claims in the Application are now in a condition for allowance, and respectfully requests allowance of such Claims.

Applicant respectfully requests that the Examiner call Applicant's attorney at the below listed number if the Examiner believes that such a discussion would be helpful in resolving any remaining problems.

Respectfully submitted,

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Purification of Single-Shell Nanotubes**

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The recent discoveries of methods^[1,2] for large-scale synthesis of single-shell nanotubes has opened the door to studying their physical and chemical properties, which are expected to be quite unique.^[3,4] However, the samples still contain large amounts of impurities (typically 30 % or more), such as amorphous carbon and catalytic metal particles, that need to be eliminated for accurate measurements, whether one studies the bulk or the individual tubes. Here we report an extremely simple and efficient method for removing most of the impurities from the nanotube samples.

It was believed that purification of single-shell nanotubes based on preferential oxidation and/or separation using surfactants was much more difficult than that of multishell nanotubes.^[5-8] For instance, gas-phase oxidation, which yields purified multishell nanotubes,^[5] destroys the single-shell nanotubes before anything else in the sample. So efforts have been directed at modifying other techniques originally developed for multishell nanotubes.^[9,10] Tohji et al.^[9] published a method using ultrasonication in water and treatment with hydrochloric acid. The yield of pure single-shell nanotubes is only 2 % of the starting material for a 48 h process. More recently, Bandow et al.^[10] reported a method mainly based on microfiltration under overpressure. A major advantage of this process is that it is driven by pure physicochemical interactions of the carbon products with the amphiphilic molecules and the filter membrane, leaving the nanotubes undamaged. The most serious drawback is the dependence of this procedure on the quality of the sample. It is known that sonicating nanotubes for a long period of time and at a high frequency can cause damage by breaking the nanotubes up into smaller pieces.^[11] We have found it hard to successfully apply this method to all samples. Typically, significant amounts of amorphous carbon and catalytic particles remain.

The one-step method presented here does not appear to be sensitive to the quality of the starting material. Moreover, it eliminates at the same time the carbonaceous material and most of the catalytic metal content.

The single-shell nanotubes were prepared by the laser-oven ablation method^[1] (see Experimental section). In this way, up to 30 mg/h of raw material could be synthesized, providing that the focused laser spot was continuously moved on the target surface to uniformly ablate the superficial material. Among all the parameters of this method, this one seems to be the most critical in order to obtain good yields. The transmission electron microscopy (TEM) pictures in Figure 1 show the quality of such raw single-shell nanotube samples. Typically, there is a mixture of ca. 50 % of bundles of single-shell nanotubes and ca. 50 % of carbonaceous material, gray graphitic nanoparticles, and black catalyst (cobalt and nickel) grains (Fig. 1a). A closer examination (Fig. 1b) of the tubes shows a layer of irregular thickness of amorphous carbon coating the bundles, which is particularly abundant where the bundles cross.

In the desire to open single-shell nanotubes with acids, we processed the raw nanotube samples in boiling concentrated nitric acid (See Experimental section). This method was developed for opening and filling multishell nanotubes by Green and co-workers.^[7] To our surprise, the nanotube sample seemed to become purer. After refluxing the sample for

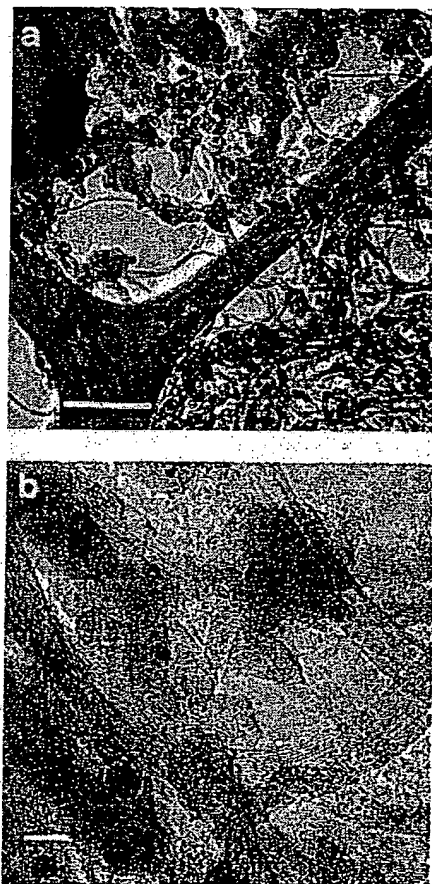
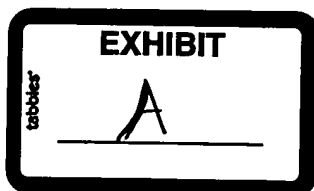


Fig. 1. TEM micrographs at low (a, scale bar 0.2 μ m) and high (b, scale bar 20 nm) magnification of as-synthesized single-shell nanotubes. Microscope Hitachi H9000-NAR, 100 kV.

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4 h in 70 % nitric acid at 120 °C, it was pure. The result of such a treatment is shown in Figures 2a and 2b. It is striking that the single-shell nanotubes appeared to be sufficiently (chemically) inert for a large proportion to survive such strongly oxidizing conditions. The yields, in terms of left-over weight of the sample after oxidation, can be as high as 50 %, which appears to reflect the initial nanotube content.

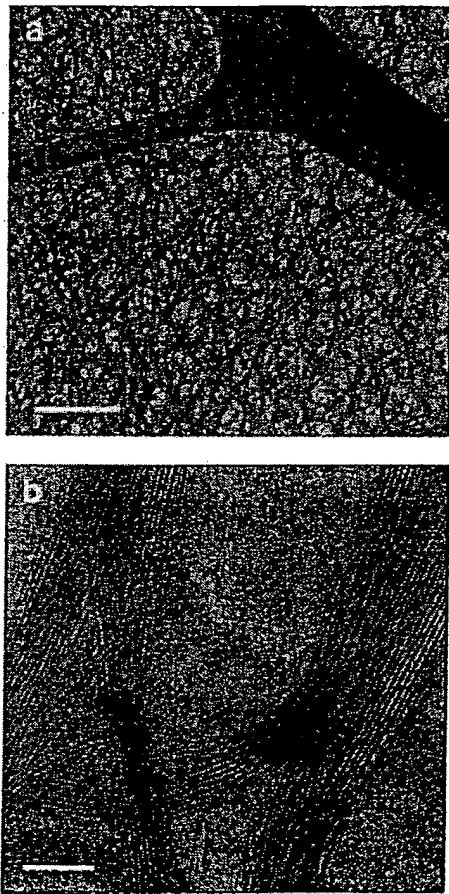


Fig. 2. TEM micrographs at low (a, scale bar 0.2 mm) and high (b, scale bar 20 nm) magnification of as-synthesized single-shell nanotubes purified by treatment in boiling nitric acid. Microscope Hitachi H9000-NAR, 100 kV. Note: The treated samples are more sensitive to the TEM beam than the original material, probably due to the presence of the oxides.

Large areas of the mat formed by the pure single-shell nanotubes on the TEM grids revealed no severe damage to the walls of the nanotubes, as shown in Figure 2b. The nitric acid not only reacts preferably with the particles but it leaves most of the tubes intact in the bundles. Occasionally one can see isolated tubes but it is very difficult to tell whether the tubes are open or not because of the low contrast of a single carbon wall. Some debris can still be seen on the outside of the bundles. Probably, after removing the impurities, the acid reacts with the outermost tubes of the bundles. In other words, the outer tubes in the bundle protect the inner ones.

In this regard, it should also be noted that no distortion or loss of contrast is visible in the TEM pictures of the walls

of the single-shell nanotubes in the purified samples. This could mean that the sp^2 structure is mostly conserved and that the amount of sp^3 carbons bearing alcohol, carboxylic or carbonyl functions is quite small. This is unlike multi-shell nanotubes, where these functional groups are found to cover the entire surface.^[6] Nevertheless, those hydrophilic groups are undoubtedly present on the purified single-shell nanotubes since the purified nanotubes are much more stable in aqueous suspensions than the raw ones. Like multishell tubes, annealing of the samples at high temperature should eliminate residual surface oxides.^[12]

Although we did not see any remaining catalytic particles in the sample, a chemical analysis was performed on the samples to quantify the amount of metal before and after purification. Interestingly, while the target contained 2 % metal (Ni and Co, total weight percent), the amount in the raw nanotube samples was 3 %. In terms of nanotube content this about 6 %, while purification leaves ca. 1 %. In other words, the metal content is reduced by a factor of six relative to the nanotube content. The 1% is still surprisingly large considering that these metals readily dissolve in the acid. We are currently trying to find ways of removing the remaining metal.

A final remark is warranted. Due to their high curvature, nanotubes pick up impurities from just standing in air or in a solvent. This can be a very fast process, occurring in a day or even less, depending on the environment. It results in the nanotubes being coated with a sheath of amorphous material, which is easily observed by TEM. Needless to say this can have significant consequences on any property measurements.

It seems clear from this study that the kinetics of the reactivity of single-shell nanotubes is different from that of both multishell nanotubes and fullerenes. In particular they are relatively inert toward oxidation by acids, at least in a bundle form. This property allows the purification of the as-synthesized mixture by this fast, high-yield, and easy to handle procedure. This is by far the simplest and most reproducible method to date for both single and multishell tubes. It should be a helpful step for further physical or chemical experiments and technological applications.

Experimental

Purification Processes: 10 mg of raw material (0.83 mmol of carbon) containing 40–60 % of single-shell nanotubes are sonicated in 5 mL of concentrated nitric acid (70 vol.-%, 87.8 mmol) with a regular monofrequency ultrasonic bath (maximum power) for a few minutes. The suspension is then refluxed under magnetic stirring at 120–130 °C for 4 h. Dense yellow vapors of nitrogen dioxide evolve during the first 3 h, indicating a high rate of oxidation of hydrocarbons into alcohols, carboxylic acids, ketones, or aldehydes, and of metallic particles of cobalt and nickel into their corresponding ions. Later, the vapors become less dense as the nitric acid probably oxidizes less-reactive species.

The suspension is then cooled and centrifuged in glass tubes at 3400 rpm for 15 min, and the resulting yellow-brown solution is decanted. The wet powder is washed with portions of 10 mL of distilled water, centrifuged (3400 rpm, 15 min), and decanted iteratively as long as the solid settles down completely in 15 min (in general two or three washing cycles). The

pH of the successive washing solutions is monitored and is about six when the suspension of single-shell nanotubes starts to be stable on the centrifugation timescale. At this point, the powder is washed twice with 15 mL portions of nitric acid and filtered on fritted glass before rinsing twice with 15 mL portions of distilled water. Between each of these steps the suspension is sonicated. Finally, the wet powder is dried and kept in a dessicator under vacuum. The overall yield ranges between 30 and 50 %.

Synthesis of Single-Shell Nanotubes: A carbon target is made by mixing 31 g of graphite cement (Dylon Industries Inc.) with 2.70 g of graphite powder (GP-G, Dylon Industries Inc.), 0.35 g of cobalt (Aldrich, powder, <2 μm , 99.8 %), and 0.36 g of nickel (Aldrich, powder, submicrometer, 99.8 %). The homogeneous mixture containing 0.3 at.-% of each catalyst is molded in a 0.75 inch quartz tube (1 inch = 2.54 cm) and baked in air for 12 h at 120 °C and for 12 h at 200 °C. The baked target is then cured at 1200 °C for 6 h in vacuum (6×10^{-2} torr). For the nanotube synthesis, the target is placed in a 1 inch quartz tube under a pressure of 500 torr of argon and a gas flow of 400 cm^3/min after several purges. The quartz tube is maintained at 1200 °C during the synthesis. A YAG-Nd laser (SEO Titan-P, 10 Hz, 230 mJ/pulse at 532 nm, 270 mJ/pulse at 1064 nm) was used to generate pulsed beams at 1064 and 532 nm. The former is delayed by 13 ns with respect to the latter. Both beams are focused to a 3–4 mm spot on the target. For optimal yield, the focal spot of the beams is moved on the target every few minutes. After the synthesis runs, the quartz tube is cooled down to room temperature under argon flow. A fine web-like deposit then collects on the walls of the quartz tube and on the cold finger that closes this tube.

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